TECHNOLOGICAL METHODS FOR BARIUM TITANATE SYNTHESIS (Review)

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Several technological methods for synthesis of ceramics based on barium titanate are considered. It is stressed that the liquid-phase synthesis methods are the most promising. The author proposes a method for liquid-phase synthesis of a precursor for barium-titanate ceramics and describes the most rational scheme of its production.

Barium titanate is important for electrical engineering. Different methods for its synthesis exist. However, not everything is clear regarding the choice of the initial chemical forms, their ratio, dispersion, and the state of the gas medium in the course of high-temperature synthesis. The classical method for production of barium-titanate ceramics [1, 2] is a lengthy labor-intensive process. Sintering is usually carried out at a temperature of 1270 – 1430°C (according to Balkevich [3], it can be done at 1300 – 1325°C); therefore, scientists are actively searching for efficient non-traditional methods for the production of barium-titanate ceramics.

According to the data in [4], the first compounds that are formed in the $BaO - TiO_2$ system are $BaTiO_3$ and Ba_2TiO_4 which have the maximum absolute value of formation enthalpy (136.6 and 144.4 kJ/mole, respectively). It was noted in [5 – 7] that the composition of the primary product mostly depends on the dispersion of TiO_2. In using TiO_2 powder with a particle size of ~ 5 μm and sintering up to the temperature of 1300 K, the primary phase is metatitanate, and when the TiO_2 particles have a size of ~ 20 μm, the primary phase is orthotitanate. However, in sintering above 1300 K, the nature of the effect of TiO_2 dispersion significantly changes: due to the high efficiency of the reaction zone on single highly disperse TiO_2 particles, the reaction between previously formed Ba_2TiO_4 and TiO_2 intesifies. As a result, an equilibrium phase composition is established: $BaTiO_3(Ba_2TiO_4) - BaTi_4O_9 - Ba_2Ti_9O_{20}$ (the Headwell effect) [8].

It is shown in [9] that at the ratio of $Ti^{4+} : Ba^{2+} \leq 1$ and with high-temperature treatment, segregation occurs on the grain surface of Ba_2TiO_4 orthotitanate mixture, which abruptly alters the sintering kinetics of phase formation and hampers ceramic sintering due to the emergence of highly disperse particles. An excess of BaO can cause transition of

$BaTiO_3$ to the hexagonal modification which is not ferroelectric [10]. In contrast, Chy and Rae [11], Gribovskii and Vcherashnaya [12] observed that with a slight excess of Ba^{2+}, finer particles of $BaTiO_3$ are formed. It has a positive effect on strengthening of ceramics and is preferable in molding of thin-wall articles. However, there is a limiting size of $BaTiO_2$ particles below which the Curie point is destabilized.

An unusual method for $BaTiO_3$ synthesis in described in [13]. The initial materials were metallic barium and titanium that were heat-treated at 300 – 900°C in pure oxygen with a gas pressure of 0.1 MPa. At the temperature of 300°C, barium peroxide Ba_2O was formed, and titanium remained in the peroxide matrix in the form of unoxidized metallic particles. At a temperature of 375 – 500°C, barium orthotitanate was formed as the result of a solid-phase reaction. Heating to 900°C produced oxidation of the residual metallic titanium, with resulting synthesis of $BaTiO_3$. The authors decided that the determining factors of metatitanate formation were the degree of grinding of the metallic barium-titanate precursor and the heating rate within the interval of 300 – 500°C.

By using the technology described in [14], it is possible to obtain a homogeneous compound with only one cycle of heat treatment. This method is distinguished by high efficiency and the possibility of molding pieces of complex configurations, but is extremely power-consuming. A reference book [15] describes the region of glass formation in the $BaO - TiO_2$ system: with a minimum content of BaO (74.2%), a compound close in composition to orthotitanate is formed.

Rice noted that in classical synthesis of $BaTiO_3$, the gas atmosphere has to be carefully controlled, since even slight impurities of chlorine can seriously slow the rate of sintering [16].

Crystalline barium titanate grown in a melt of solvent salts is used for specific purposes, for example, as modulators in laser physics [10, 17, 18].

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The use of $CaTiO_3$, $SrTiO_3$, or an excess of TiO_2 (~ 5 mol. %) for the purpose of predominant crystallization of $BaTiO_3$ in cubic syngony was described in [10]. Special attention was paid to the gas medium: a reducing or inert atmosphere has a negative effect on synthesis of barium titanate. Efficient solvent salts include $BaCl_2$, KF, NaF, BaF_2, PbO, Na_2CO_3, Li_2SiO_3, Na_2SiO_3, K_2SiO_3. Synthesis was carried out in platinum crucibles, and in the case of $BaCl_2$, alundum cricibles were used.

The authors in [16] reported growth of $BaTiO_3$ crystal in a melt of $NaKCO_3$ salt at the temperature of 800°C.

The Remeika method [19] is used for the production of $BaTiO_3$ in the form of thin plates. The crystals are grown in platinum crucibles in KF melt at a temperature of ~ 1100°C. The method is distinguished by high labor intensity and requires extreme thoroughness, since the slightest deviation from the procedure results in failure.

At present, liquid-phase chemical synthesis has the priority. Research is mostly directed toward obtaining precursors which are later used for ceramic production.

A relatively simple and popular method consists in precipitation and coprecipitation of barium titanate in aqueous and non-aqueous media. V. V. Klimov et al. used TiO_2 and $BaCl_2$ or $Ba(NO_3)_2$ (USSR Inventor's Certificate No. 159809). Titanium oxide was obtained by mixing $TiCl_4$ and H_2O_2. After cooling this mixture to 10 – 15°C, NH_4OH and barium salt solution were added. As a consequence, a finely crystalline precipitate was obtained, dried, calcined at a temperature of 800 – 1000°C, and sintered until a ceramic was produced.

The study in [20] describes a number of methods for synthesis of barium titanate. Gram and Patterson used $BaTiO_3$ synthesized as a result of the reaction between barium and titanium hydroxides in boiling in a nitrogen current. It is recommended to use oxalic and tartaric acid in precipitation in order to keep in solution such undesirable impurities as Fe, Si, Al, and Na.

The specific variants of the oxalate method differ in the conditions of isolation of barium titanyl oxalate $BaTiO(2O_4)_2 \cdot 4H_2O$ (BTO) from aqueous solution and its thermal decomposition [20]. Clabot isolated BTO by adding a mixture of barium and titanium chloride solutions to oxalic acid at a temperature of 80 – 85°C with subsequent calcination of the precipitate at 900 – 1000°C for 20 h. Lind and Merker obtained BTO by adding barium chloride to titanyl oxalic acid at a temperature of 65 – 70°C. The preipitate was calcined at the temperature of 900°C for 3 h, $BaTiO_3$ was obtained as powder with 0.1 – 0.6-μm particles passing on a No. 015 sieve. Strizhkov et al. isolated BTO in the same way as the former authors but without heating, the precipitate was calcined at the temperature of 850°C and sintered at 1240 – 1360°C. Kiss and Magde synthesized BTO by boiling barium titanate previously sintered from $BaCO_3$ and TiO_2 for 20 h in 10% oxalic acid. Calcination was carried out at 650 – 1150°C, and different fractions of the compound were obtained depending on the temperature.

In the tartrate method of $BaTiO_3$ production [20], synthesis of titanyl tartrate $BaTiO(C_4H_4O_6)_2$ proceeded in acqueous medium, and in calciantion at the temperature of 600°C it be-

came $BaTiO_3$. The powder particles could pass through a No. 015 sieve.

Several methods for synthesis of barium titanate using alcoholates are known. The methods differ mostly in the kind of alcohol used and the pyrolysis conditions. Several methods are discussed in [20]. Barium titanate was isolated as the result of boiling barium methylate and titanium ethalate. After separation, the precipitate was calcined at the temperature of 1600 K and material particles 0.02 – 0.05 μm in size were obtained. Sometimes, simple 2 – 11-atom alcohols are used. It was reported that isolation of alcoholates from water-alcohol solutions was performed by alcohol distillation or hydrolysis with addition of ammonia or by passing water vapor through the solution. The precipitates thus obtained were calcined at a temperature of 400 – 800°C. $BaTiO_3$ powder of the 0.1 – 0.2 μm fraction was obtained in a hot chamber in combustion of alcohol solutions at the temperature of 430°C. Walsh carried out pyrolysis similarly to the former method but used a mixture of ethylates and carbon salts of barium and titanium. Combustion was performed at the temperature of 800 – 1200°C at a temperature of 800 – 1200°C. Spherical particles nearly 4 μm in size were obtained.

The alcohol methods described above used "distillation" titanium tetrachloride with a low content of Fe, Si, Al, and V impurities (< 0.005%) as the initial titanium-bearing component. Different authors used barium chlorides, nitrates, hydrochlorides or metallic barium for obtaining barium alcoholates.

According to Mehrotra [2], a promising line of research is the use of bimetallic alkoxides, such as $BaTi(OEt)_6$ (EtOH — ethyl alcohol), especially in production of films.

In [22], the author describes a variant of film production involving the use of titanium tetraisopropylate solution in isopropanol. The solution was aged at room temperature for 30 min, and then barium acetate was added in a molar ratio of [Ba] : [Ti] equal to 1. The synthesized coumpound was heat-treated at 600°C.
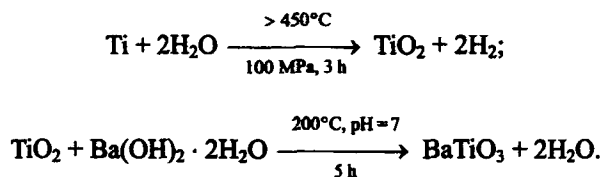
An interesting method for production of crystalline $BaTiO_3$ of tetragonal modification is described in [23]. Metallic barium reacted with isopropyl alcohol in benzene medium to which titanium tetraisopropoxide $Ti[OCH(H_3)]_4$ was added. The molar ratio of metal alcoholates was 1 : 1. The reacting mixture was held in argon medium at the temperature of 45°C up to complete dissolution of the barium, then held at room temperature for several days for crystal formation. Crystals isolated from the solution (access of CO_2 and water vapor was completely excluded) were heat-treated at 100 – 1000°C. The authors stated that $BaTi[OCH(CH_3)_2]_6 \cdot xC_6H_6$ crystals formed in the benzene medium, and at the temperature of 100°C, the bimetallic alcoholate was converted to a form of tetragonal $BaTiO_3$. However, the best results were obtained at the temperature of 800°C.

Larbot et al. [24] used BaO or $Ba(OH)_2 \cdot 8H_2O$ dispersed in methanol and titanium tetraisopropylate or tetrabutylate as initial materials to obtain perovskite, $BaTiO_3$. A mixture of the components was hydrolyzed and then a gel formed. The gel was dried at the temperature of 100°C, sintering was conducted at 1200 – 1300°C. The authors concluded that an in-

crease in the temperature of solid-phase synthesis had a positive effect on compaction of the ceramics, but the electrical properties of the products deteriorated.

Original technology for $BaTiO_3$ production was developed by Kumar and Messing [25]. Titanium isopropoxide was dissolved in a mixture of citric acid and ethylene glycol, and then $BaCO_3$ was added. In this case, the ratio of Ba : Ti was maintained equal to 1 : 1. A solution of the ingredients heated to 90°C acquired a bright yellow color. Further heating produced an increase in the viscosity and variation in color, as a consequence a vitreous dark brown resin was obtained. This material was heat-treated at 375°C, and final thermolysis was carried out at 700°C. First, exothermic oxidation occurred in air with the resulting formation of ultrafine bimetallic oxycarbonate, which later endothermically decomposed into $BaTiO_3$.

The technology of hydrothermal synthesis developed by Rice is of interest [16]:

$$Ti + 2H_2O \xrightarrow[\text{100 MPa, 3 h}]{> 450°C} TiO_2 + 2H_2;$$

$$TiO_2 + Ba(OH)_2 \cdot 2H_2O \xrightarrow[\text{5 h}]{200°C, pH = 7} BaTiO_3 + 2H_2O.$$

We likewise developed a method for liquid-phase synthesis of a precursor. We investigated schemes involving butyl and isopropyl alcohols, as well as the aqueous-hydrochloric acid scheme with addition of hydrogen peroxide and ammonium. The synthesis was monitored by the pH-meter method. The correlation-regression analysis of the experimental data made it possible to optimize the synthesis procedure: select the quantitative and qualitative composition of the mixture, the methods of external effect, as well as to identify the role of the reactants in the different stages of synthesis. As a result, the most rational scheme for producing a precursor for barium-titanate ceramics was chosen. The pH-meter control and relatively simple method of mathematical processing can be successfully used in circumstances when complicated and expensive analytical investigations of the structure of a compound cannot be applied [26].

To conclude, it should be noted that the importance of ceramics based on barium titanate for electrical engineering is inducing researchers to search for optimum methods of its synthesis. The analysis of the extensive data does not allow for categorical identification of the optimum conditions for production of barium titanate: the chemical forms of the initial materials, the preliminary treatment methods, the temperature conditions of synthesis, its duration, the composition of the gas medium, etc. However, liquid-phase synthesis is presumably the most promising, since a compound similar in its crystal chemical properties to the end product can be obtained as early as in the precursor stage.

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